Microstructure and properties that change during hard cyclic visco-plastic deformation of bulk high purity niobium

Lembit Kommel

Department of Mechanical and Industrial Engineering, Tallinn University of Technology, Ehitajate tee 5, 12618 Tallinn, Estonia

A R T I C L E   I N F O

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A B S T R A C T

The effect of strain amplitude and strain rate on the microstructure and the properties that change during hard cyclic visco-plastic deformation of bulk niobium of high purity at room temperature are systematically measured. These changes in the refractory metal niobium were studied at different tension-compression strain amplitudes (up to $E = \pm 2\%$) and strain rates (up to $\dot{\varepsilon} (1) = 0.4 \text{ s}^{-1}$) during hard cyclic visco-plastic deformation in dependence on von Mises strain (up to $E_{\text{vm}} = 13.8$) during the equal channel angular pressing, respectively. The pure Nb was specified with respect to microstructure, micromechanical properties, density, gas content, tensile strength, Young's modulus, viability and fracture mechanics at fatigue failure for use in industry. The micro hardness and the indentation modulus of the nanostructured shear bands were significantly higher, but the plasticity was lower than that of the body metal between the shear bands. The decreasing Young's modulus (when increasing the strain rate) is related to the fatigue failure of the niobium during the tension-compression cycling and shows nucleation and thickening of the shear bands, as well as the changes in grain boundaries in the pre-fracture state.

1. Introduction

The high purity niobium (Nb) is an important refractory metal for the production of radiofrequency accelerating superconducting (SCRF) cavities [1-3] and superconducting sheets [4], pressure tubes in nuclear reactors [5], chemical process industry [6] and heat shield of the antennas for the Solar Orbiter space missions [7] and so on. The SCRF cavities performance is sensitive to the microstructure, physical and chemical properties of Nb. To use the Nb in these applications, the microstructure, and the previous properties were modified by severe plastic deformation techniques. To refine the as-cast microstructure and change the mechanical, physical and chemical properties of Nb, severe plastic deformation (SPD) techniques have now been widely used [8]. During SPD in metals, grain size decreases under simple shear stress caused by compression or hydrostatic pressure [9]. The most popular SPD technique is equal channel angular pressure (ECAP) [10]. Compared to the high-pressure torsion technique (HPT), ECAP is an industrial SPD process for the structuring of relatively large sample materials [11]. It is well known from research so far [8-11] that immediately after ECAP metals with ultrafine grain microstructure (UFG) experience higher tension stress, exhibit higher hardness, high dislocation density, but lower thermal stability and decreased plasticity compared to its coarse grained (CG) and fine-grained (FG) counterparts. It is indicated in [12-14] that the electrical conductivity of pure Nb depends on the sample orientation and dislocation density. How the non-metallic elements (C, H, N, O2) influence the mechanical properties (decrease the hardness and ductility), it is not clear for Nb [12,15,16, and]. The GB wetting modes whether complete, partial or pseudo partial, as well as the GB faceting-roughness, have been studied by Straumal et al. [17-19]. In these studies it was proved that the GB wetting is very sensitive to the temperature and pressure of SPD processing and depends on the chemical composition of the alloy. In particular, the unusual mechanical and other properties of the multi-component alloys after SPD were controlled not only by the grain size itself but also by the structure and properties of the grain boundaries (GB). Even in one-component materials such as high purity Nb, the GB phase transitions can take place, especially in the twin GB that frequently built the majority of the material GB population during SPD. It is proposed (but not studied yet) that enriched GB films can increase the super plasticity properties of UFG alloys and control electrical conductivity. At present, mechanical properties change of metals have been tested at different cyclical frequencies, such as ultra-low cycle fatigue (LCF) [20], high cycle fatigue (HCF) [21] and ultrasonic fatigue testing (UFT) [22]. The impact on the fatigue life prediction at small strain amplitudes but with high strain ratio has been studied by Chaboche et al. in [23]. However, these investigations have shown that the
microstructure of metals does not change during such viability tests, only cracks initiation and their prolongation at time and fracture mechanics are studied. The well-known test methods to examine the viability of materials are ratcheting [24] (soft cyclic visco-plastic deformation, which does not contain compression cycle). The tension-compression cycling or hard cyclic visco-plastic deformation (HCVD) [25] is based on the Bauschinger effect [26] and is characterized by very low cycle numbers (up to 20–30) and the application of large tension-compression constant strain amplitude (up to $\varepsilon = \pm 2.5\%$). According to this method the influence of strain amplitude and strain rate of HCVD on the evolution of microstructure and micromechanical properties of bulk high purity Nb are researched in present study. The mechanisms of reduction of cyclical hardening - softening, change of the Young’s modulus, damage by fatigue at HCVD and fracture mechanics were systematically studied under given different processing (ECAP and HCVD) parameters. The test results are discussed in terms of the corresponding microstructural evolution and changes in micromechanical properties of SB-s in pure Nb.

2. Experimental procedures

2.1. Material and preparation of samples

In this study, the double electron-beam melted (EBM) pure bulk Nb ingots were co-opted for experimental tests. The EBM pure Nb ingots with a diameter of 210 mm were obtained from Neo Performance Materials Silmet (Molycorp Silmet AS), Estonia. The pure Nb ingots cast after electron beam melting had a columnar microstructure up to 15–20 cm in length and approximately 5–6 cm in thickness. The chemical analysis of Molycorp Silmet AS showed that the high purity Nb metal ingots contained the following non-metallic elements: N (30 ppm), O (72 ppm), H (< 10 ppm), C (< 20 ppm), and metallic elements: Ta (160 ppm), Si (< 20 ppm), P (< 15 ppm), Mo (< 10 ppm) and W + Mo (< 20 ppm), respectively. The microstructure of the pure Nb ingot after EBM also contained many micro pores. We propose that gases H, O, and N are not only detected dissolved in the matrix as interstitials, as well as in micro pores, which were not vacuumed and were partly filled with gases atoms. Material with such structure and properties not suitable for the production of SCRF cavities, pressure tubes in nuclear reactors, chemical process industry and heat shield of the antennas for the Solar Orbiter space missions [1–7] and so on. For experimental work the ingots obtained were cut into samples of $12 \times 12$ mm in cross-section and 130 mm in length and used for microstructure and properties change in Nb. The samples were subjected to heat treatment for homogenization of the microstructure in a vacuum oven at 1200 °C for 2 h. Fifteen samples were considered adequate for the ECAP and HCVD techniques. The samples were then subjected to ECAP in a die with channels crossing at 90° angles without radii at the intersection of the channels. Before processing by ECAP, the samples were covered with copper film and molybdenum disulfide grease (MoS2) to lowering the friction coefficient (COF) and the Nb galling to the surface of the ECAP die channels. The samples for the test were subjected to ECAP by the B route during 1, 2, 4, 6, 8, 10 and 12 passes, respectively. The corresponding von Mises strains ($\varepsilon_{\text{VM}}$) were 1.15, 2.3, 4.6, 6.9, 9.2, 11.5 and 13.8, respectively. The samples were correspondingly indexed as E1, E2, E4, E6, E8, E10 and E12. The ECAP processing was carried out at room temperature. During processing, the temperature of the shear region was increased up to $\sim 200$ °C as a result of heating by severe deformation and extrusion at a speed of 5 mm·s$^{-1}$. The test samples for HCVD were cut off and had cross-section diameters of 9.9 mm and a corresponding cross-sectional area of 77 mm². The samples were tested on an Instron-8516, which is used for HCVD tests. In particular, the triangular strain control test method was used. This technique involves tension-compression cycles at $\pm 0.1\%$, $\pm 0.2\%$, $\pm 0.5\%$, $\pm 1\%$, $\pm 1.5\%$ and $\pm 2.0\%$ of strain amplitudes for 20 cycles at a constant frequency of $f = 0.5$ Hz per level of tension, respectively. The strain rate gradient was increased step by step by gradually increasing the strain amplitude ($\varepsilon$, %), deformation speed ($\nu$, mm·s$^{-1}$) and strain rate ($\dot{\varepsilon}(t)$, s$^{-1}$). The true strain in the sample during HCVD was measured with an extensometer with a base length of 10 mm in the middle part of the sample. The HCVD technique was used to study the hardening-softening behavior of the material, the evolution of the microstructure and the viability of the tested Nb metal as well as the dependence of the viability in the microstructure. The Young’s modulus in tension (0–0.1%) was measured after ECAP and after each cycling step of HCVD for 20 cycles as minimum of three times. The Young’s modulus was measured at strain rates within $\dot{\varepsilon}(t) = 0.02$ s$^{-1}$ to $\dot{\varepsilon}(t) = 0.4$ s$^{-1}$, respectively.

2.2. Microstructural analysis

The microstructure of the obtained samples was studied by optical microscopy (Nikon CX), electron microscopy (SEM) (Zeiss EVO MA-15, Gemini LEO Supra 35), transmission electron microscopy (TEM) (EVM-100BR), Spectroscopy Dispersive Energy (EDS) and X-ray diffraction (XRD, DS005 Bruker) techniques. The samples for TEM were cut by a SEM-FIB instrument (FEI Company Helios NanoLab). The test surfaces of the samples were first mechanically ground and then ground with a diamond paste; then, the samples were cleaned by ion gridding using a precision etched coating system (model 682) at 30 kV for 30 min in a protective atmosphere of argon (Ar). The chemical composition of SB was studied by SEM-EDS research.

2.3. Testing of micromechanical and physical properties

Tensile stress, density and electrical conductivity were measured, including their dependence on microstructure, strain and strain rate, respectively. The micromechanical properties of the samples (in the shear bands and between the shear bands of the metal body) were measured by nano-indentation under loads of 20 mN for 100 times crossed with shear bands direction using a nano-indentation device from the NanoTest NTX testing centre (Micro Materials Ltd.). The evolution of material density during processing was measured using OHAUS Scout-Portable scales. The O2, N and H gases contents were measured by the ELTRA ONH-2000 gaseous impurities analyzer, and the carbon content was measured by a CS-800 analyzer. The electrical conductivity of Nb was measured 30 times automatically by a Sigma test 2.069 (Foerster) according to the standards of the National Physics Laboratory (NPL, United Kingdom). The dislocation density changing was calculated (according to the XRD measures results) by use Rechinger method.

3. Results and discussion

3.1. Evolution of the Nb microstructure during ECAP

As seen in Fig. 1a, the EBM of high purity niobium metal as a cast area contains very large grains with millimeters of dimensions that are connected by fully wetted triple grain boundaries (GB). Such width of GB-s is in nanometers since the metal is Nb of high purity; it is not a multicomponent alloy having the thin layers of grain boundary, as shown in [17–19]. Unfortunately, such large grains contain pores with dimensions in micrometers (Fig. 1b). Under hydrostatic pressure in ECAP die, these pores are compressed to zero. The pores and GB defects can be completely wetted by hydrostatic compression and simple shear stresses [8,9]. The distortions induced in the formation of shear bands in the body of the sample [12]. After 4 pressing ($\varepsilon_{\text{VM}} = 4.6$), the ECAP sample submitted to the B route showed 2–3 μm grains in cross section in the shear plane (SP) region with sliding lines (SL) in grains under the orientation of $\sim 24^\circ$ (Fig. 1c). The SL in the grains is the orientation as in the sample at the corner about 24° with respect to the X axis or towards the metal flow direction in the outlet channel of the ECAP die.
After the strain increased to $\varepsilon_{TM} = 13.8$ at 12 passes, the UFG microstructure with HAGB mainly contained grain sizes of 200-250 nm (Fig. 1d). As demonstrated by Vinogradov et al. [11] in our FEM simulation, such metal flow orientation depends on the shape of the outer corner of the ECAP die and the von Mises strain (as well corresponding compression stress and friction during pressing distribution) in the deformation SP zone of ECAP die.

### 3.2. HCVD features and benefits

The proposed HCVD test method [25] was used to study the viscoplastic behavior of SPD-treated UFG metals and alloys. The summary test time of HCVD is relatively short, such as the working time of the rocket engine. The independence of the strain amplitude allows the test material to exhibit different elastic, visco-elastic and visco-plastic behaviors. All samples were analyzed in HCVD for 20 cycles, with a frequency of $f = 0.5$ Hz, in a test time of 40s, respectively. During the cycle, metals and alloys generally exhibit complete visco-elastic behavior at strain amplitudes of $\varepsilon = \pm 0.1\%$ and $\varepsilon = \pm 0.2\%$ (Fig. 2a).

Increasing the strain amplitude of the material by $> 0.5\%$, it shows visco-plastic behavior. As shown in (Fig. 2b), the strain-stress curve represents the hysteresis loop containing the plastic part. According to the increase in strain amplitude and deformation rate, the HCVD strain-stress loop width increases (Fig. 2c). Triangular strain loading with a frequency of $f = 0.5$ Hz was used in all tests during HCVD (Fig. 2d). During cycling with low strain amplitude up to $\varepsilon = \pm 0.2\%$, the time-stress curves have a triangular view identical to the time-strain curve. The maximum deformation was found in the maximum strain amplitude of $\varepsilon = \pm 2.0\%$ and corresponded to the deformation per cycle with 0.4 mm in an extensometer gauge length of 10 mm in the first and second cycle of HCVD. As you can see in (Fig. 2e), the time-stress curves show that during a compression cycle the stress decreases sharply (C $\sim$ 500 MPa) in the compression cycle and increases sharply (T $\sim$ 500 MPa) in the tensile cycle. The analysis of time-stress amplitude curves shows that the maximum value of the tensile stress is 702 MPa in the second cycle and 685 MPa at the end of the 20th cycle. The value of the compression stress was 733 MPa in the second cycle and 693 MPa in the last compression cycle, respectively. As you can see, the material softening occurred and was approximately 5.6% in the E12 sample during HCVD for 20 cycles. The maximum deformation (with a maximum deformation amplitude of $\varepsilon = \pm 2.0\%$) was $\pm 0.2$ mm on a gauge length of 10 mm. The cycling frequency was $f = 0.5$ Hz and the one cycle was performed for 2 s. As you can see (Fig. 3a), a tensile stress (mean value of 20 cycles) was increased by the strain rate $\dot{\varepsilon}(t)$ increasing for all test samples that have different microstructures and mechanical properties received during ECAP before. The maximum stress in the compression cycle has values approximately identical to those of the tension cycle. Samples E2 and E4 show an increase in stress up to the strain rate of $\dot{\varepsilon}(t) = 0.4$ s$^{-1}$, while samples E8 and E12 show a decrease in stress at a strain rate greater than $\dot{\varepsilon}(t) = 0.3$ s$^{-1}$. The tensile stress that decreased during 20 cycles was maximum for sample E6 at a strain of $\varepsilon = \pm 2.0\%$. The tensile stress decreased by about 16% and the compression stress decreased by around 12% for cycling for 20 cycles or for the time of 40 s. As you can see in (Fig. 3b) the Young’s module was increased to 105 GPa in ECAP and then during HCVD decreased to 99 GPa for sample E10 ($E_{VM} = 11.5$). In summary, during 100 cycles (at strain rate increase) the Young module was decreased for all samples with UFG microstructure before HCVD. According to this result (decrease of Young’s modulus during HCVD), we can conclude at the beginning that the interatomic interaction powers were reduced [14], respectively. In samples E6–E12 the Young module during ECAP was increased from $E_6 = 95$GPa to $E_{10} = 105$GPa and then decreased to $E_{12} = 89$ GPa, respectively. During the observed HCVD, the Young module was reduced by approximately 3% for the E8 sample and the maximum decrease of around 10% for the E12 sample was received in this study. The SB Indentation modulus at nano-indentation was significantly higher than in the body metal (Fig. 3c). As you can see, HCVD has a great influence on the mechanical properties of bulk pure UFG Nb samples, as well as on the micromechanical properties of SB and GB. The changes in the mechanical properties were measured based on the

\[\text{Fig. 1. Optical images of triple grain boundary (a) and pores (b) in EBM as-cast Nb, SEM pictures of microstructure evolution in the shear region of ECAP die at } E_{VM} = 4.6 \text{ (c), and UFG microstructure formed at } E_{VM} = 13.8 \text{ (d).}\]
evolution of the microstructure during ECAP and thereafter HCVD. The influence of SPD processing characteristics on the microstructure and the formation of Nb properties are described in our previous work [14]. The maximum tensile stress $\delta = 890$ MPa at the elongation of 2.5% occurred in sample E12 that had not been cyclically deformed by HCVD previously. Next (after HCVD) these samples were fractured with tensile stress inside $\delta = 550$ MPa to $\delta = 596$ MPa and elongation inside of 50% to 76%, respectively. As shown in our previous work [13], tensile stress during HCVD was increased only for samples with coarse-grained microstructure. During such SPD, the changes of gas content in pure bulk

![Fig. 2. HCVD curves for the viscoelastic tension-compression straining at an amplitude of $\varepsilon = \pm 0.1\%$ and corresponding deformation amplitude of $\nu = \pm 0.01$ mm in the base length of 10 mm (a), viscoelastic tension-compression straining at strain amplitude of $\varepsilon = \pm 0.5\%$ and $\nu = \pm 0.05$ mm (b) and at strain amplitude of $\varepsilon = \pm 2.0\%$ with the corresponding deformation amplitude of $\nu = \pm 0.2$ mm (c). The sample E12 HCVD time-deformation (d) and time-stress (e) curves received at $\varepsilon = \pm 2\%$ of strain amplitude. The effect of the elastic-plasticity of Nb on the deflection of the curves during the compression (C) and tension (T) cycles is shown by arrows.]

![Fig. 3. The ECAP samples tensile strength increases as the strain rate increases during HCVD (a), the Young module increases as the von Mises strain increases in ECAP (blue) and by the Young Module decrease in the ECAP samples in HCVD by 100 cycles (red) of samples Nb (b) and decrease of the Indentation module of sample E12 in HCVD (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

<table>
<thead>
<tr>
<th></th>
<th>O, ppm</th>
<th>H, ppm</th>
<th>N, ppm</th>
<th>C, ppm</th>
<th>C, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG (SC)</td>
<td>255.14</td>
<td>18.41</td>
<td>1.8</td>
<td>–</td>
<td>0.014</td>
</tr>
<tr>
<td>FG</td>
<td>202.85</td>
<td>13.01</td>
<td>0.0</td>
<td>–</td>
<td>0.011</td>
</tr>
<tr>
<td>UFG</td>
<td>127.09</td>
<td>15.33</td>
<td>0.0</td>
<td>–</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 1 The gas concentration changes in O₂, N, H, and C depending on the processed microstructure.
Table 2
The micromechanical properties between SB on body meal and SB (black lines) of sample E12 after ECAP and sample E12 after ECAP + HCVD.

<table>
<thead>
<tr>
<th>Processing</th>
<th>NH, GPa</th>
<th>Er, GPa</th>
<th>ERP</th>
<th>W_{plast}, nJ</th>
<th>W_{elast}, nJ</th>
<th>CC, nm/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>E12</td>
<td>3.02</td>
<td>124.7</td>
<td>0.085</td>
<td>4.33</td>
<td>0.89</td>
<td>2.75</td>
</tr>
<tr>
<td>E12, SB</td>
<td>4.78</td>
<td>177.7</td>
<td>0.097</td>
<td>3.56</td>
<td>0.74</td>
<td>2.42</td>
</tr>
<tr>
<td>E12 + HCVD</td>
<td>2.66</td>
<td>102.9</td>
<td>0.092</td>
<td>5.01</td>
<td>0.98</td>
<td>3.18</td>
</tr>
<tr>
<td>E12 + HCVD, SB</td>
<td>3.29</td>
<td>111.4</td>
<td>0.107</td>
<td>4.45</td>
<td>1.01</td>
<td>3.29</td>
</tr>
</tbody>
</table>

Nb occur and the results are presented in Table 1. As you can see, the content of gases in EBM pure Nb changes depending on the induced strain, and strain rate as well as the microstructure that was formed during treatment. As it can be seen, the samples with UFG microstructure have a minimum oxygen concentration and fine grain (FG) microstructure samples have reduced concentrations of hydrogen and carbon. Thus, during the SPD, the density of the EBM pure Nb increased from \( d = 8.3 \text{ g/cm}^3 \) to \( d = 8.65 \text{ g/cm}^3 \), as the pores (see Fig. 1b) of the metal were compressed. During ECAP, the dislocation density increased from \( 5 \times 10^4 \) to \( 2 \times 10^5 \) \[14\] and the micro-hardness increased from \( 100 \text{ HV}_{0.05} \) to \( 250 \text{ HV}_{0.05} \), but the electrical conductivity decreased from 6.74 MS/m (at the beginning ECAP pressing) at 6.6 MS/m, respectively. The micromechanical properties of Nb were measured by nano-indentation technique under a load of 20 mN (Table 2). The polished surface has approximately 27% more nano-hardness and indentation modulus than samples with additional chemical etching. We studied the samples that were diamond polished and chemically etched with HNO3: HF 1:1. The chemical etching reduced the Vickers nano-hardness (NH, GPa), the elastic modulus (Er, GPa), the elastic recovery parameter (ERP) and the plastic part of the indentation work (\( W_{plast}, \text{nJ} \)) but reduces the contact compliance parameter (CC, nm/Mn) values, respectively. The results of the nano-indentation of SB and metallic body (between SB) are presented in Table 2. The elastic part of the indentation work (\( W_{elast}, \text{nJ} \)) during the FCAP decreased, but during the next HCVD, these parameters increased, respectively. The samples after HCVD in tensile tests show increasing plasticity properties. Parameters such as NH, Er, and ERP were significantly increased but parameters such as \( W_{plast} \) and \( W_{elast} \) were reduced during ECAP and HCVD. The contact compliance parameter (CC) and the elastic work (\( W_{elast} \)) of the indentation were increased during HCVD. Such changes in mechanical, physical and chemical properties we will characterize with changes in the microstructure of Nb in the next chapter of this study.

3.3. SB-s microstructure evolution during HCVD

The evolution of the microstructure and the formation of secondary SB during HCVD as a function of the strain rate and the deformation amplitude are studied. The optical and TEM images of the microstructures in a diametrical section of samples after HCVD and after ECAP for comparison are shown in Fig. 4. At first, the intersecting SB forming were detected at \( \epsilon_s = \pm 1.5\% \) of the strain amplitude and at the corresponding strain rate of \( \dot{\epsilon}(t) = 0.3 \text{ s}^{-1} \) at the HCVD. This sample

![Fig. 4.](image-url)
was deformed cyclically before at lower deformation amplitudes ($\varepsilon_1 = \pm 0.1\%$, $\varepsilon_2 = \pm 0.2\%$, $\varepsilon_3 = \pm 0.5\%$ and $\varepsilon_4 = \pm 1.0\%$ for 20 cycles, respectively). The investigated SB-s at increased magnification is shown in SEM pictures (Fig. 5a, c, d) and in TEM picture (Fig. 6b), respectively. The SB has high dislocation density (Fig. 6b) and nanostructure (Fig. 6c, d). The material after ECAP shows a non-homogeneous microstructure, as well as micromechanical properties. The SEM-EDS investigation of SC and Nb body metal between SB shows that the chemical content was identical as the high purity Nb metal was tested. We conclude that the differences in the micromechanical properties of SB and metallic body are related to the evolution of the microstructure. The nanostructured SB-s were stable to chemical etching. As shown before, the SB takes shape in the SP region by pressing for the first time through ECAP. Then, during the processing of HCVD, the SB evolves. The samples of Nb after ECAP at $\varepsilon_{VM} = 9.2 \div 11.5$ contain dislocation lines with high density in TEM picture (Figs. 4d and 5b). They have a higher hardness and lower plasticity properties compared to the body metal between SB-s. At higher magnification, this process is shown in SEM images (Fig. 5a) and in TEM images (Fig. 5b). The investigated SB-s nanostructure is shown in Fig. 5c and in high magnification in Fig. 5d. Such SB has nanostructure and high micromechanical properties (see Table 2, row E12, SB).

### 3.4 Fracture mechanics

The microstructure of SB after ECAP (at $\varepsilon_{VM} = 13.8$) and HCVD (for 5 test series at strain rate increasing and for summary 100 cycles) was sampled before pre-fatigue failure state after the softening of material during HCVD, at the end of HCVD test, the cracks were formed by SB-s (Fig. 6a). The SB contains blocks with a thickness of approximately 100–200 nm and width up to 500 nm (Fig. 6b). The length of the blocks was not measured. These blocks are stable against chemical etching (Fig. 6c). Cracking occurs through such places. After such complete processing and testing, the samples were sent for tensile tests up to the fracture. The corresponding fracture surfaces for sample E12 are presented after ECAP (Fig. 7a) and after HCVD (Fig. 7b). The fracture surfaces presented have identical characters for all samples from E6 to E12. As you can see in Fig. 7a and b, differences are added in the result of processes that take place in GB-s during HCVD. The SEM image (Fig. 7c) shows the GB fracture in the Nb metal sample. This phenomenon of microstructure and properties change in the pre-fracture state during HCVD will enrich the material science of viability and
fracture mechanics of pure metals during exploitation in different applications.

4. Summary and concluding remarks

A series of experiments were carried out to investigate the effect of von Mises strain ($\varepsilon_{vM}$) during ECAP, axial compression-tension deformation with gradual increase of strain ($\varepsilon(t)$) or deformation amplitude and increase of the corresponding strain rate ($\dot{\varepsilon}(t)$) during HCVD on microstructure, physical, chemical and mechanical properties of pure bulk Nb. Then, a series of experiments were conducted to investigate the effects of strain, axial deformation and strain rate during HCVD on the microstructure and the properties evolution in the pre-failure state of pure bulk Nb. The comparative analysis was carried out and the following conclusions can be drawn from this study:

1. ECAP and HCVD result in a step-by-step refinement of the Nb microstructure from SC to the UFG structure in Nb and NC microstructures on SB of Nb.
2. During SPD processing of EBM as-cast Nb samples, the pores and any defect in GB-s at hydrostatic compression pressure concurrently with simple shear stress were eliminated.
3. The density of pure Nb increased from 8.27 g/cm$^3$ in as-cast condition to 8.65 g/cm$^3$ after ECAP and HCVD processing’s, or higher then theoretical (8.55 g/cm$^3$) density.
4. During the following HCVD, the nanostructure (20–90 nm) was formed in shear bands.
5. The electrical conductivity during ECAP decreased and during HCVD it increased in the result of the dislocation density decreasing from 5E + 10 cm$^{-2}$ to 2E + 11 cm$^{-2}$ since the dislocations are the mine obstacles for electrons mowing [12,13].
6. During ECAP, Young's modulus was increased to 105 GPa in the von Mises strain $E_{vM} = 11.5$ and then decreased to 99 GPa during the HCVD. The Young modulus (89 GPa) was minimal for sample E12 after HCVD at strain amplitude ($\varepsilon$ = ± 2.0%).
7. In this study, it is shown that the softening of the material is related to the decrease of Young's modulus at the HCVD with the increase of the strain rate higher then $\dot{\varepsilon}(t) = 0.3$ s$^{-1}$.
8. In turn, the decrease in Young's modulus indicates a decrease in the attraction of interatomic force in the Nb metal [12].
9. The micromechanical properties differ for ECAP and HCVD samples, as well as for SB and in body metal. For example, after ECAP for 12 passes per B$_2$ route, the SB maximal Vickers nano-hardness was NH = 4.78GPa and the indentation modulus was Er = 177.7 GPa. During the following HCVD, these parameters were reduced to NH = 3.29 GPa and Er = 111.4 GPa, respectively.
10. The GB width of pure Nb is so small that it is not possible to measure its micromechanical properties by the nano-indentation method used in present study.
11. The gases content in Nb depend on microstructure condition. It is minimal for UFG pure Nb.
12. Compared to the LCM and HCF tests, the HCVD tests require a shorter timeframe.

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